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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PURPOSE: To improve a charge/discharge cycle characteristic by decreasing carbon packing density in an internal surface side carbon layer of a negative pole, so that compression force between carbon materials at charge time is decreased to suppress the carbon layer from collapsing and the carbon material from falling off.

CONSTITUTION: A prescribed amount of natural graphite is dispersed in a binding agent solution to adjust two kinds of slurry of different graphite concentration so that packing density of a carbon layer obtains 1.12g/cc and 1.40g/cc. Respectively different two kinds of slurry is applied to both

surfaces of copper foil as negative pole collector and dried, to prepare a negative pole 2, and the carbon layer, placing the surface of smaller carbon packing density in the inside, is wound with a positive pole 1 and a separator 3, to form a battery BA1 impregnated with a prescribed electrolyte. Thus by decreasing carbon packing density in an internal surface side carbon layer of the negative pole smaller than that of an outer side carbon layer by 5 to 20%, compression force of the negative pole at charge time is weakened, to prevent the carbon layer from collapsing and carbon material from falling off, and a charge/discharge characteristic can be improved.

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CLAIMS

[Claim(s)]

[Claim 1] the nonaqueous electrolyte rechargeable battery characterize by for the negative electrode with which spreading formation of the carbon layer [both sides of a charge collector] which can occlusion emit a lithium ion be carried out to have make carbon pack density of the carbon layer by the side of the inside of said negative electrode smaller 5 to 20% than the carbon pack density of the carbon layer by the side of the external surface of said negative electrode with the separator which estrange a positive electrode and these positive/negative two poles in the nonaqueous electrolyte rechargeable battery which be roll round at a curled form and it come to contain in a cell can.

[Claim 2] LiCoO_2 , LiNiO_2 , and LiMnO_2 Or LiFeO_2 Nonaqueous electrolyte rechargeable battery according to claim 1 used as positive active material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of the negative electrode aiming at raising a cycle property in detail with respect to the nonaqueous electrolyte rechargeable battery which uses a carbon material as a negative-electrode ingredient.

[0002]

[Description of the Prior Art] since a nonaqueous electrolyte rechargeable battery does not need to take the decomposition voltage of water into consideration in recent years unlike the drainage system rechargeable battery which uses the **** water electrolytic solutions, such as a nickel cadmium rechargeable battery, a high-voltage design is possible -- etc. -- it is brought into the limelight from a reason.

[0003] As a negative-electrode ingredient of this kind of cell, although the metal lithium was used conventionally, it inquires recently as new materials which carbon materials which only carry out occlusion emission of the lithium ion at the time of the charge and discharge in which very such [being pointed out] a problem does not have the badness of the cycle property based on growth of an arborescence electrocrystallization lithium, such as corks and a graphite, replace with a metal lithium.

[0004] The nonaqueous electrolyte rechargeable battery which uses this carbon material as a negative-electrode ingredient has the outstanding cycle property, and in addition, since discharge capacity is also large (for example, the initial discharge capacity of a graphite is about 370 mAh/g.), it is a cell expected as a next-generation power source for portable devices.

[0005] However, since a crack occurs and collapsed in a carbon layer or a carbon material exfoliates and was omitted from a negative electrode in it with expansion and contraction of the negative electrode at the time of charge and discharge, while piling up the charge-and-discharge cycle, there was a problem that discharge capacity fell gradually in this cell. That is, there was room which should improve further about a cycle property.

[0006] The above-mentioned problem was remarkable in the cylindrical cell which carries out the laminating of the positive/negative two poles through a separator, whirls around (spiral), rolls these round to a **, and is especially contained and assembled in a cell can.

[0007] Then, as a result of inquiring wholeheartedly about the cause, when this invention persons have a cause in having used the equal negative electrode of the carbon pack density of each carbon layer by which spreading formation was carried out and the ratio of the carbon pack density of each carbon layer was improved, they hit on an idea for the above-mentioned problem to be solved.

[0008] This invention is made based on this knowledge, and the place made into the

purpose is to offer the nonaqueous electrolyte rechargeable battery which discovers the cycle property which was excellent since omission from collapse of the carbon layer at the time of charge and discharge and the negative electrode of a carbon material hardly took place.

[0009]

[Means for Solving the Problem] The nonaqueous electrolyte rechargeable battery (the "this invention cell" is called hereafter.) concerning this invention for attaining the above-mentioned purpose The negative electrode with which spreading formation of the carbon layer which can occlusion emit a lithium ion was carried out to both sides of a charge collector with the separator which estranges a positive electrode and these positive/negative two poles It is rolled round by the curled form, sets to the nonaqueous electrolyte rechargeable battery which it comes to contain in a cell can, and is a carbon layer by the side of the inside of said negative electrode (an "inside side carbon layer" is called hereafter.). About carbon pack density, it is a carbon layer by the side of the external surface of said negative electrode (an "external surface side carbon layer" is called hereafter.). It is characterized by having made it smaller 5 to 20% than carbon pack density.

[0010] The cell which this invention uses as an amelioration plug is a nonaqueous electrolyte rechargeable battery which the negative electrode which uses a carbon material as a negative-electrode ingredient is rolled round by the curled form with a positive electrode and a separator, and it comes to contain in a cell can.

[0011] In this kind of cell, the carbon material in an inside side carbon layer receives compressive force mutually, and, on the other hand, the carbon material in an external surface side carbon layer receives tensile force mutually. and -- the time of charge and discharge -- the carbon material in which carbon layer -- equal -- a lithium ion -- occlusion -- or it is going to emit, and is going to expand or contract. However, the carbon material in an inside side carbon layer cannot expand, if the expansion force at the time of charge does not overcome compressive force, but when compressive force is larger than expansion force, omission from collapse of a carbon layer or the negative electrode of a carbon material take place. The above is conventionally imagined to be the reason which was not good in a cell.

[0012] So, by this invention cell, carbon pack density of an inside side carbon layer was made to make it smaller than the carbon pack density of an external surface side carbon layer. The reason whose cycle property improves by doing in this way is that expansion becomes possible [without the carbon material in an inside side carbon layer receiving compressive force so much mutually at the time of charge] since carbon pack density is

small.

[0013] The reason to which it was presupposed that carbon pack density of an inside side carbon layer is made smaller 5 to 20% than that of an external surface side carbon layer is as follows. That is, although the compressive force which it commits between carbon materials when the compressive force committed between carbon materials cannot fully be eased and 20% is exceeded, although the contact resistance between carbon materials in less than 5% of case becomes small is eased, it is because the contact resistance between carbon materials becomes large and neither of the cases is desirable on a cell property. the value which ²(ed) weight of the carbon material contained in a carbon layer by the volume of the whole carbon layer with carbon pack density here -- saying -- a negative electrode -- a mixture -- it is adjusted by adjusting the amount of the carbon material blended with inside.

[0014] Thus, this invention has the description at the point to which it was presupposed that the negative electrode with which the carbon pack density of each carbon layer formed in both sides differs is used, in order to obtain the nonaqueous electrolyte rechargeable battery excellent in the cycle property. So, it is possible to use it without a limit of the various ingredients which are not restricted especially about other members which constitute cells, such as a positive-electrode ingredient and the electrolytic solution, are conventionally used as an object for nonaqueous electrolyte rechargeable batteries, or are proposed.

[0015] For example, as a positive-electrode ingredient (active material), they are LiCoO₂, LiNiO₂, LiMnO₂, and LiFeO₂. It is mentioned as a suitable thing.

[0016] moreover -- as the electrolytic solution -- the mixed solvent of organic solvents, such as ethylene carbonate, vinylene carbonate, and propylene carbonate, these, and low-boiling point solvents, such as dimethyl carbonate, diethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, and ethoxy methoxyethane, -- LiPF₆, LiClO₄, and LiCF₃ SO₃ etc. -- 0.7-1.5M (a mol/liter), and the melted solution out of which 1M came comparatively above all are illustrated in an electrolytic-solution solute.

[0017]

[Function] In this invention cell, since the negative electrode with the carbon pack density of an inside side carbon layer smaller 5 to 20% than that of an external surface side carbon layer is used, it can expand, without a negative electrode receiving so big compressive force at the time of charge. For this reason, even if it piles up a charge-and-discharge cycle, it decreases that a carbon layer collapses or a carbon material is omitted from a negative electrode.

[0018]

[Example] It is possible to change this invention suitably in the range which is not limited at all by the following example and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0019] (Example 1) AA -- the nonaqueous electrolyte rechargeable battery (this invention cell) of a mold (AA) was produced.

[0020] [Positive electrode] LiCoO₂ as positive active material After having made the 5-% of the weight N-methyl pyrrolidone (NMP) solution of polyvinylidene fluoride distribute the mixture which mixed and obtained the artificial graphite as an electric conduction agent by the weight ratio 9:1, preparing the slurry and applying this slurry to both sides of the aluminium foil as a positive-electrode charge collector with a doctor blade method, the vacuum drying was carried out by 100-degreeC for 2 hours, and the positive electrode was produced. Incidentally, each active material pack density by the side of the inside of this positive electrode and external surface was 2.6g/cc.

[0021] [Negative electrode] Two sorts of slurries from which the 5-% of the weight NMP solution of the polyvinylidene fluoride as a binder is made to distribute the natural graphite of the specified quantity, and graphite concentration differs were prepared so that the carbon pack density of a carbon layer might be set to cc in 1.12g [cc] /or 1.40g /. Subsequently, after applying the slurry with the above-mentioned high graphite concentration to one side of the copper foil as a negative-electrode charge collector and applying a slurry with the above-mentioned low graphite concentration to the field of another side with a doctor blade method, respectively, the vacuum drying was carried out by 100-degreeC for 2 hours, and the negative electrode was produced.

[0022] The [electrolytic solution] It is LiPF₆ to the constant volume mixed solvent of ethylene carbonate and dimethyl carbonate. It melted at a rate of 1M and the electrolytic solution was prepared.

[0023] [production of a cell] -- the above positive/negative two poles and electrolytic solution -- using -- AA -- this invention cell BA 1 of a mold (AA) was produced. However, the field with smaller carbon pack density was *****ed inside, and rolling up of a negative electrode rolled it round. In addition, as a separator, the fine porosity film made from polypropylene (the product made from SERANIZU, trade name "Celgard") was used, and the previous electrolytic solution was infiltrated into this.

[0024] Drawing 1 is the sectional view (each cell which carries out a postscript is also an isomorphism-like cell.) showing the produced this invention cell BA 1 typically, and the cell BA 1 of illustration consists of the separator 3 which estranges a positive electrode 1, a negative electrode 2, and these two electrodes, the positive-electrode lead

4, the negative-electrode lead 5, a positive-electrode external terminal 6, a negative-electrode can 7, etc. The positive electrode 1 and the negative electrode 2 are held in the negative-electrode can 7, after having been rolled round by the curled form through the separator 3 into which the nonaqueous electrolyte was poured, and through the positive-electrode lead 4, for the positive-electrode external terminal 6, it can connect with the negative-electrode can 7 through the negative-electrode lead 5, and they can take [a positive electrode 1] out a negative electrode 2 now to the exterior again by making into electrical energy chemical energy produced inside the cell.

[0025] (Example 2) The carbon pack density of an inside side carbon layer produced this invention cell BA 2 like the example 1 except having used the negative electrode whose carbon pack density of 1.20g [cc] /and an external surface side carbon layer is 1.40g/cc.

[0026] (Example 3) The carbon pack density of an inside side carbon layer produced this invention cell BA 3 like the example 1 except having used the negative electrode whose carbon pack density of 1.26g [cc] /and an external surface side carbon layer is 1.40g/cc.

[0027] (Example 4) The carbon pack density of an inside side carbon layer produced this invention cell BA 4 like the example 1 except having used the negative electrode whose carbon pack density of 1.30g [cc] /and an external surface side carbon layer is 1.40g/cc.

[0028] (Example 1 of a comparison) The comparison cell BC 1 was produced like the example 1 except having used the negative electrode each whose carbon pack density of an inside side carbon layer and an external surface side carbon layer is 1.40g/cc.

[0029] (Example 2 of a comparison) The carbon pack density of an inside side carbon layer produced the comparison cell BC 2 like the example 1 except having used the negative electrode whose carbon pack density of 1.35g [cc] /and an external surface side carbon layer is 1.40g/cc.

[0030] (Example 3 of a comparison) The carbon pack density of an inside side carbon layer produced the comparison cell BC 3 like the example 1 except having used the negative electrode whose carbon pack density of 1.10g [cc] /and an external surface side carbon layer is 1.40g/cc.

[0031] [Rate of cycle degradation of each cell] After charging to charge termination electrical-potential-difference 4.1V by 200mA, the cycle trial which makes 1 cycle the process which discharges to discharge-final-voltage 2.75V by 200mA was performed, and the rate of cycle degradation of each cell to a 500 cycle eye was compared. A result is shown in drawing 2 .

[0032] drawing 2 -- the rate of cycle degradation of each cell -- an axis of ordinate -- the rate of cycle degradation to a 500 cycle eye (%/cycle) -- moreover, it is the graph by which the carbon pack density (g/cc) of the inside side carbon layer of the negative electrode of each cell was taken and shown on the axis of abscissa. It is shown what % value shown on the axis of abscissa by parenthesis writing has the carbon pack density of each inside side carbon layer smaller than that of an external surface side carbon layer. Moreover, the rate of cycle degradation is the value which broke the ratio (%) of the discharge capacity of the 500 cycle eye to the discharge capacity in early stages of a cycle by 500 cycles.

[0033] This drawing shows that the carbon pack density of an inside side carbon layer compares this invention cells BA1-BA4 which used the negative electrode made smaller 5 to 20% than that of an external surface side carbon layer with the comparison cells BC1-BC3 which used the negative electrode of a specification which separates from the above-mentioned range, and the rate of cycle degradation to a 500 cycle eye is small excellent in a cycle property.

[0034] an above-stated example -- this invention -- AA -- although the case where it applied to a mold cell was explained, especially a limit does not have this invention cell in the configuration, and it can be applied to the nonaqueous electrolyte rechargeable battery of other various configurations, such as a flat mold and a square shape.

[0035] Moreover, although polyvinylidene fluoride was used as a binder in the example, it is also possible to use other binders, such as polyimide.

[0036] Furthermore, although the example explained the cell which made only the carbon pack density of the carbon layer of both sides of a negative electrode differ, the cell which has the further excellent cycle property can be produced by making the active material pack density of each active material layer further formed in both sides of a positive electrode differ.

[0037] Although the cell which used the liquid electrolyte was mentioned as the example and the example explained it further again, this invention can be applied also to a solid electrolyte cell.

[0038]

[Effect of the Invention] The characteristic effectiveness excellent in it being rare for a carbon layer to collapse or for a carbon material to be omitted from a negative electrode, even if it piles up a charge-and-discharge cycle, since the negative electrode only with a predetermined rate smaller than that of the carbon layer by the side of external surface is used for the carbon pack density of the carbon layer by the side of an inside by this invention cell as explained in full detail above, and excelling in a cycle property for this

reason, etc. and this invention is done so.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the AA type this invention cell.

[Drawing 2] It is the graph which shows the rate of cycle degradation of each cell produced in the example and the example of a comparison.

[Description of Notations]

BA1 This invention cell

1 Positive Electrode

2 Negative Electrode

3 Separator